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(54) HEAT TRANSFER TUBE FOR WASTE HEAT BOILER UTILIZING WASTE INCINERATION EXHAUST GAS, EXCELLENT IN HIGH TEMPERATURE CORROSION RESISTANCE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a heat transfer tube for a waste heat boiler utilizing waste incineration exhaust gas, excellent in high temp. corrosion resistance and particularly in high temp. intergranular corrosion resistance.

SOLUTION: This heat transfer tube composed of an Ni-Cr-base alloy which has a composition consisting of 38-50% Cr, 0.1-2% of Mo and/or W, 0.001-0.05% C, 0.001-0.1% Mg, 0.001-0.1% B, and the balance Ni with Si, P, and S, as inevitable impurities, limited to ≤ 0.1%, ≤0.03%, and ≤0.03%, respectively, and further containing, if necessary, the following (a) and/or (b): (a) one or ≥2 kinds among 0.001-0.1% of rare earth elements, 0.001-0.1% Y, 0.001-0.1% Zr, and 0.001-0.5% Hf; (b) either or both of 0.01-1.0% Mn and 0.001-0.1% Ca.

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(54)【発明の名称】高温耐食性に優れたごみ焼却排ガス利用廃熱ボイラの伝熱管

(57)【要約】

【課題】　高温耐食性、特に高温耐粒界腐食性に優れたごみ焼却排ガス利用廃熱ボイラの伝熱管を提供する。

【解決手段】　Ｃｒ：３８～５０％、ＭｏおよびＷのうちの１種または２種：０．１～２％、Ｃ：０．００１～０．０５％、Ｍｇ：０．００１～０．１％、Ｂ：０．００１～０．１を含有し、さらに必要に応じて下記の（ａ）および／または（ｂ）を含有し、残りがＮｉと不可避不純物からなり、不可避不純物としてＳｉ：０．１％以下、Ｐ：０．０３％以下、Ｓ：０．０３％以下に制限した組成を有するＮｉ－Ｃｒ基合金で構成した伝熱管。（ａ）希土類元素：０．００１～０．１％、Ｙ：０．００１～０．１％、Ｚｒ：０．００１～０．１％、Ｈｆ：０．００１～０．５％の内の１種または２種以上。（ｂ）Ｍｎ：０．０１～１．０％、Ｃａ：０．００１～０．１％の内の１種または２種。

【特許請求の範囲】

【請求項１】　重量％で、Ｃｒ：３８～５０％、ＭｏおよびＷのうちの１種または２種：０．１～２％、Ｃ：０．００１～０．０５％、Ｍｇ：０．００１～０．１％、Ｂ：０．００１～０．１を含有し、残りがＮｉと不可避不純物からなり、不可避不純物として含まれるＳｉ、ＰおよびＳをそれぞれＳｉ：０．１％以下、Ｐ：０．０３％以下、Ｓ：０．０３％以下に制限した組成を有するＮｉ－Ｃｒ基合金で構成したことを特徴とする高温耐食性に優れたごみ焼却排ガス利用廃熱ボイラの伝熱管。

【請求項２】　重量％で、Ｃｒ：３８～５０％、ＭｏおよびＷのうちの１種または２種：０．１～２％、Ｃ：０．００１～０．０５％、Ｍｇ：０．００１～０．１％、Ｂ：０．００１～０．１を含有し、
さらに、希土類元素：０．００１～０．１％、Ｙ：０．００１～０．１％、Ｚｒ：０．００１～０．１％、Ｈｆ：０．００１～０．５％の内の１種または２種以上を含有し、残りがＮｉと不可避不純物からなり、不可避不純物として含まれるＳｉ、ＰおよびＳをそれぞれＳｉ：０．１％以下、Ｐ：０．０３％以下、Ｓ：０．０３％以下に制限した組成を有するＮｉ－Ｃｒ基合金で構成したことを特徴とする高温耐食性に優れたごみ焼却排ガス利用廃熱ボイラの伝熱管。

【請求項３】　請求項１または２記載のＮｉ－Ｃｒ基合金に、さらにＭｎ：０．０１～１．０％、Ｃａ：０．００１～０．１％の内の１種または２種を含有したＮｉ－Ｃｒ基合金で構成したことを特徴とする高温耐食性に優れたごみ焼却排ガス利用廃熱ボイラの伝熱管。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】この発明は、高温耐食性、特に高温耐粒界腐食性に優れたごみ焼却排ガス利用廃熱ボイラの伝熱管に関するものである。

【０００２】

【従来の技術】一般に、ごみ焼却施設には排ガスのもつ高温潜熱を利用する目的で、廃熱ボイラが設置されている。また、前記廃熱ボイラの構造部材である伝熱管は、腐食性の強いＨＣｌやＳＯ$_2$ガス、Ｎａ$_2$ＳＯ$_4$などの溶融硫酸塩、さらにＮａＣｌやＫＣｌなどの溶融塩化物などの腐食性生成物を含有する高温の排ガスにさらされ、かつ前記硫酸塩や塩化物などの一部が表面に堆積した状況下におかれることから、その製造には耐食性の優れた材料が用いられている。

【０００３】耐食性の優れた材料の一つとして、重量％で（以下、％は重量％を示す）、Ｃｒ：３８～５０％、ＭｏおよびＷのうちの１種または２種：０．１～２％を含有し、さらに必要に応じて、、希土類元素：０．００１～０．１％、Ｙ：０．００１～０．１％、Ｚｒ：０．１～３％、Ｈｆ：０．１～３％の内の１種または２種以上を含有し、不純物として含まれるＣおよびＮをそれぞれＣ：０．０５％以下、Ｎ：０．０４％以下に制限し、残りがＮｉおよびその他の不可避不純物からなる組成を有するＮｉ－Ｃｒ基合金が知られている（特開平１－１３２７３２号公報参照）。

【０００４】

【発明が解決しようとする課題】この従来の特開平１－１３２７３２号公報記載のＮｉ－Ｃｒ基合金は、各種の酸に対しては優れた耐食性を示すが、ごみ焼却による腐食性の強いＨＣｌやＳＯ$_2$ガス、Ｎａ$_2$ＳＯ$_4$などの溶融硫酸塩、さらにＮａＣｌやＫＣｌなどの溶融塩化物などの腐食性生成物を含有する高温の排ガスにさらされ、かつ前記硫酸塩や塩化物などの一部が表面に堆積する複雑な状況下においては、十分な高温耐食性を示さず、従って、この従来のＮｉ－Ｃｒ基合金で構成したごみ焼却排ガス利用廃熱ボイラの伝熱管は、高温耐食性が不足し、そのために使用寿命が短かった。

【０００５】

【課題を解決するための手段】そこで、本発明者等は、上述のような観点から、より一段と優れた高温耐食性を有するＮｉ－Ｃｒ基合金を開発し、この高温耐食性に優れたＮｉ－Ｃｒ基合金を用いて一層使用寿命の長いごみ焼却排ガス利用廃熱ボイラの伝熱管を開発すべく研究を行なった結果、（イ）　従来の特開平１－１３２７３２号公報記載のＮｉ－Ｃｒ基合金に、Ｍｇ：０．００１～０．１％およびＢ：０．００１～０．１を共に含有せしめると、熱間加工性が優れると共に高温耐粒界腐食性が向上したＮｉ－Ｃｒ基合金が得られ、このＮｉ－Ｃｒ基合金で構成したごみ焼却排ガス利用廃熱ボイラの伝熱管は、従来の特開平１－１３２７３２号公報記載のＮｉ－Ｃｒ基合金で構成した伝熱管に比べて高温耐粒界腐食性が優れているところから、結果として排ガス雰囲気中での高温耐食性が一層向上し、伝熱管の寿命が一層伸びる、（ロ）　希土類元素：０．００１～０．１％、Ｙ：０．００１～０．１％、Ｚｒ：０．００１～０．１％、Ｈｆ：０．００１～０．５％のうちの１種または２種以上を含有せしめると、熱間加工性が向上するので好ましい、（ハ）　Ｍｎ：０．０１～１．０％、Ｃａ：０．００１～０．１％の内の１種または２種を含有すると、Ｎｉ－Ｃｒ基合金の脱酸が行われるところから耐食性が一層向上する、などの研究結果が得られたのである。

【０００６】この発明は、上記の研究結果にもとづいてなされたものであって、Ｃｒ：３８～５０％、ＭｏおよびＷのうちの１種または２種：０．１～２％、Ｃ：０．００１～０．０５％、Ｍｇ：０．００１～０．１％、Ｂ：０．００１～０．１を含有し、さらに、必要に応じて、（ａ）希土類元素：０．００１～０．１％、Ｙ：０．００１～０．１％、Ｚｒ：０．００１～０．１％、Ｈｆ：０．００１～０．５％の内の１種または２種以上、（ｂ）Ｍｎ：０．０１～１．０％、Ｃａ：０．００

１～０．１%の内の１種または２種、以上、（ａ）および／または（ｂ）を含有し、残りがＮｉと不可避不純物からなり、不可避不純物として含まれるＳｉ、ＰおよびＳをそれぞれＳｉ：０．１%以下、Ｐ：０．０３%以下、Ｓ：０．０３%以下に制限した組成を有するＮｉ－Ｃｒ基合金で構成した高温耐食性、特に高温粒界腐食性に優れたごみ焼却排ガス利用廃熱ボイラの伝熱管に特徴を有するものである。

【０００７】この発明の伝熱管を構成するＮｉ－Ｃｒ基合金の成分組成を上記の通りに限定した理由を説明する。

（ａ）　Ｃｒ

Ｃｒ成分には、ＭｏおよびＷと共存した状態で高温のごみ焼却排ガスに対する高温耐食性および高温耐酸化性を向上させると共に、高温強度を向上させる作用があるが、その含有量がＣｒ：３８%未満になると前記作用に所望の効果が得られず、一方、Ｃｒ含有量が５０%を越えると脆化し、成形加工時に割れが生じやすくなるところから、その含有量を３８～５０%、望ましくは４３～４７%に定めた。この組成範囲でＣｒ基のα相の析出は少ないほど好ましく、Ｃｒ基のα相の析出は面積比で１０%以下にすることにより最大の耐食性と加工性を得ることができる。

【０００８】（ｂ）　ＭｏおよびＷ

これら成分は、共に素地に固溶し、Ｃｒと共存した状態で耐食性を向上させる作用があるが、その含有量が０．１%未満では前記作用に所望の耐食性向上効果が得られず、一方その含有量が２%を越えると成形加工性が低下するようになることから、その含有量を０．１～２%、望ましくは０．５～１．５%と定めた。

【０００９】（ｃ）　Ｃ

Ｃ成分は高温強度を向上させる作用があるが、その含有量が０．００１%未満では所望の高温強度を確保することができず、一方、Ｃ成分の含有量が０．０５%を越えると、粒界に存在する炭化物の量が増大するようになって、特に高温排ガス中に含有する溶融塩化物による粒界腐食の進行が促進されるようになることから、その含有量を０．００１～０．０５%と定めた。

【００１０】（ｄ）　Ｍｇ

Ｍｇ成分には、高温耐粒界腐食性を向上させ、かつ熱間加工性も向上させる作用があるが、その含有量が０．００１%未満では所望の効果が得られず、一方その含有量が０．１%を越えると粒界に金属化合物を生成し、熱間加工性および高温耐粒界腐食性が低下するようになることから、その含有量を０．００１～０．１%、望ましくは０．００１～０．０５%と定めた。

【００１１】（ｅ）　Ｂ

Ｂ成分には高温耐粒界腐食性を向上させる作用があるが、その含有量が０．００１%未満では所望の効果が得られず、一方その含有量が０．１%を越える粒界に硼化合物を生成し、高温耐粒界腐食性を低下するようになることから、その含有量を０．００１～０．１%、望ましくは０．００１～０．０１%と定めた。

【００１２】（ｆ）　希土類元素、Ｙ、Ｚｒ、Ｈｆ

これらの成分には、熱間加工性を向上させる作用があるので必要に応じて含有させるが、その含有量が、いずれかの成分も０．００１%未満では所望の熱間加工性向上効果が得られず、一方、希土類元素、ＹおよびＺｒにあっては０．１%、Ｈｆにあっては０．５%を越えても熱間加工性をより一層の向上させる効果が得られないことから、その含有量を、希土類元素：０．００１～０．１%、Ｙ：０．００１～０．１%、Ｚｒ：０．００１～０．１%、Ｈｆ：０．００１～０．５%と定めた。

【００１３】（ｇ）　Ｍｎ、Ｃａ

ＭｎおよびＣａには脱酸作用があり、ＭｎおよびＣａ添加による脱酸によって、Ｎｉ－Ｃｒ基合金の耐食性を一層向上させるので必要に応じて添加するが、その含有量はＭｎ成分で０．０１%、Ｃａ成分で０．００１%未満では前記作用に所望の効果が得られず、一方、その含有量がＭｎ成分で１．０%を越え、Ｃａ成分で０．１%を超えると、それらの析出相が生成し、熱間加工性および耐食性が低下することから、その含有量はそれぞれＭｎ：０．０１～１．０%、Ｃａ：０．００１～０．１%に定めた。

【００１４】（ｈ）　不可避不純物

不可避不純物としてＳｉ、Ｐ、Ｓ、ＴｉおよびＡｌを含有する場合があるが、Ｓｉ成分の含有量が０．１%を越えると靭性が低下するようになり、ＰおよびＳがそれぞれＰ：０．０３%およびＳ：０．０３%を越えると、粒界に偏析するようになって熱間加工性を低下させかつ高温耐粒界腐食性も低下させ、ＴｉおよびＡｌの含有量がそれぞれ０．４%を越えると熱間加工性が損なわれるようになる。したがって、Ｓｉ、Ｐ、Ｓ、ＴｉおよびＡｌはそれぞれＳｉ：０．１%以下、Ｐ：０．０３%以下、Ｓ：０．０３%以下、Ｔｉ：０．４%以下、Ａｌ：０．４%以下にとどめなければならない。

【００１５】

【発明の実施の形態】つぎに、この発明の伝熱管を実施例により具体的に説明する。通常の高周波溶解炉を用いて、表１～４に示される成分組成をもったＮｉ－Ｃｒ基合金溶湯を調製し、インゴットに鋳造し、このインゴットに１０００～１２５０℃の範囲内の所定温度で熱間鍛造を施して直径：６５㎜の丸棒材とし、ついでこの丸棒材から直径：６０㎜×肉厚：５㎜の寸法に削り出すことにより本発明伝熱管１～３５および従来伝熱管１～５をそれぞれ製造した。

【００１６】ついで、この結果得られた各種の伝熱管を廃熱ボイラに組み込み、この廃熱ボイラを処理能力：２００ton／日のごみ焼却施設に設置し、前記伝熱管の表面温度：５５０℃、排ガス温度：６７０℃の条件で１８

５

００時間の操業を行ない、操業終了後伝熱管を取り出し、表面に付着した灰分や生成スケールを除去した状態で周方向における肉厚を測定して最大減肉量を求めると共に、表面部の断面ミクロ組織を観察して最大粒界腐食

６

長さを測定し、これらの結果を表５に示した。

【００１７】

【表１】

種別		成分組成（重量%）										
		Cr	Mo	W	C	Mg	B	Si	P	S	その他	Ni+不純物
本発明伝熱管	1	38.2	0.5	0.9	0.034	0.042	0.005	0.045	0.015	0.008	－	残
	2	44.9	1.0	0.2	0.026	0.039	0.005	0.036	0.010	0.011	－	残
	3	49.8	0.5	1.7	0.036	0.028	0.002	0.078	0.016	0.017	－	残
	4	45.2	0.3	0.8	0.002	0.027	0.009	0.059	0.007	0.021	－	残
	5	45.8	0.6	0.7	0.047	0.025	0.006	0.008	0.019	0.012	－	残
	6	44.8	0.7	0.2	0.027	0.002	0.006	0.015	0.018	0.019	－	残
	7	44.7	0.5	0.4	0.030	0.098	0.007	0.026	0.025	0.014	－	残
	8	44.8	1.0	0.2	0.025	0.026	0.002	0.032	0.009	0.016	－	残
	9	44.9	0.3	0.6	0.039	0.036	0.097	0.039	0.016	0.023	－	残
	10	45.2	0.2	－	0.028	0.029	0.004	0.043	0.020	0.018	－	残

【００１８】

【表２】

種別		成分組成（重量%）										
		Cr	Mo	W	C	Mg	B	Si	P	S	その他	Ni+不純物
本発明伝熱管	11	44.8	1.8	－	0.027	0.032	0.006	0.018	0.015	0.019	－	残
	12	44.7	－	0.2	0.030	0.048	0.007	0.025	0.016	0.014	－	残
	13	44.8	－	1.9	0.025	0.026	0.002	0.009	0.002	0.016	－	残
	14	44.9	0.1	0.1	0.029	0.036	0.007	0.018	0.009	0.023	－	残
	15	45.2	1.2	0.7	0.028	0.029	0.004	0.020	0.003	0.018	－	残
	16	46.6	1.0	0.5	0.021	0.033	0.008	0.074	0.009	0.011	La:0.045, Ce:0.021	残
	17	45.8	0.6	1.0	0.019	0.029	0.005	0.015	0.011	0.024	Y:0.071	残
	18	45.6	－	1.5	0.036	0.031	0.009	0.009	0.012	0.008	Zr:0.068	残
	19	45.1	－	1.2	0.028	0.021	0.008	0.045	0.014	0.019	Hf:0.15	残
	20	46.4	1.4	－	0.022	0.029	0.006	0.016	0.011	0.012	La:0.078, Y:0.023	残

【００１９】

【表３】

7　8

種別		成分組成（重量%）										
		Cr	Mo	W	C	Mg	B	Si	P	S	その他	Ni+不純物
本発明伝熱管	21	44.4	1.6	−	0.027	0.024	0.008	0.012	0.013	0.011	Ce:0.078, Hf:0.091	残
	22	45.1	0.9	0.7	0.023	0.031	0.004	0.009	0.020	0.012	La:0.066, Zr:0.047	残
	23	46.5	0.8	0.3	0.038	0.029	0.009	0.021	0.025	0.022	Y:0.041, Hf:0.11	残
	24	44.2	1.4	0.2	0.025	0.027	0.003	0.011	0.029	0.024	La:0.033, Y:0.0071, Hf:0.083	残
	25	45.2	0.6	1.2	0.029	0.030	0.009	0.012	0.029	0.015	Ce:0.012, Y:0.074, Zr:0.074	残
	26	44.8	1.2	−	0.034	0.045	0.008	0.012	0.022	0.011	La:0.0074, Hf:0.082, Zr:0.056	残
	27	45.8	1.4	−	0.028	0.032	0.002	0.039	0.018	0.021	Ce:0.0074, Hf:0.082, Zr:0.0056, Y:0.0047	残
	28	46.0	1.0	0.5	0.019	0.034	0.007	0.023	0.024	0.008	Mn:0.82	残
	29	45.6	0.8	0.8	0.021	0.025	0.008	0.021	0.016	0.012	Ca:0.081	残
	30	45.2	−	1.3	0.036	0.029	0.007	0.016	0.009	0.021	Mn:0.14, Ca:0.031	残

【００２０】　【表４】

種別		成分組成（重量%）										
		Cr	Mo	W	C	Mg	B	Si	P	S	その他	Ni+不純物
本発明伝熱管	31	44.9	1.1	−	0.028	0.030	0.002	0.046	0.020	0.013	Mn:0.66, Y:0.062, Ca:0.072	残
	32	45.1	0.8	0.5	0.033	0.033	0.003	0.028	0.020	0.010	Mn:0.72, La:0.092, Y:0.034	残
	33	45.3	0.5	0.7	0.080	0.035	0.004	0.043	0.015	0.015	Ca:0.042, Hf:0.22, Y:0.054	残
	34	45.3	0.6	0.3	0.044	0.041	0.008	0.022	0.013	0.012	Mn:0.32, La:0.083, Hf:0.12, Ca:0.078, Y:0.026	残
	35	45.8	0.9	0.4	0.032	0.028	0.007	0.014	0.017	0.011	Mn:0.20, Y:0.013, Hf:0.088, Ca:0.019, Zr:0.025	残
従来伝熱管	1	38.7	1.5	0.2	0.031	−	−	−	−	−	N:0.032	残
	2	45.3	0.6	0.5	0.028	−	−	−	−	−	N:0.025	残
	3	45.5	0.4	1.1	0.022	−	−	−	−	−	N:0.019	残
	4	46.2	−	1.7	0.013	−	−	−	−	−	N:0.027	残
	5	45.6	1.5	−	0.024	−	−	−	−	−	N:0.030	残

（＊印：本発明範囲外）

【００２１】　【表５】

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種別		最大減肉量（mm）	最大粒界腐食長さ（mm）
本発明伝熱管	1	0.29	0.11
	2	0.25	0.08
	3	0.28	0.10
	4	0.26	0.10
	5	0.26	0.09
	6	0.26	0.09
	7	0.27	0.10
	8	0.26	0.09
	9	0.27	0.09
	10	0.28	0.10
	11	0.28	0.11
	12	0.29	0.10
	13	0.28	0.10
	14	0.28	0.09
	15	0.28	0.09
本発明伝熱管	16	0.25	0.09
	17	0.25	0.08
	18	0.26	0.09
	19	0.26	0.09
	20	0.26	0.09
	21	0.26	0.09
	22	0.25	0.09
	23	0.25	0.08
	24	0.25	0.09
	25	0.25	0.09
	26	0.25	0.09
	27	0.26	0.08
	28	0.24	0.08
	29	0.24	0.08
	30	0.24	0.07
本発明伝熱管	31	0.24	0.07
	32	0.25	0.08
	33	0.25	0.08
	34	0.23	0.07
	35	0.23	0.07
従来伝熱管	1	0.38	0.15
	2	0.37	0.13
	3	0.37	0.15
	4	0.38	0.16
	5	0.35	0.13

【００２２】

【発明の効果】表１～５に示される結果から、本発明伝熱管１～３５は、従来伝熱管１～５に比べて高温のごみ焼却排ガス雰囲気に従来より長持間さらされても、最大減肉量が少なくかつ最大粒界腐食長さが格段に短いところから、優れた高温耐食性、特に優れた高温耐粒界腐食性を示すことが分かる。

【００２３】上述のように、ＭｇおよびＢを微量を添加したこの発明の伝熱管は、従来よりも一段と優れた高温耐食性を示すので、ごみ焼却による廃熱を有効に利用するための廃熱ボイラの伝熱管の一層の長寿命化が可能となり、ごみ焼却による廃熱を有効に利用するための廃熱ボイラの技術の向上に大いに貢献し得るものである。

* NOTICES *

Bibliography

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* NOTICES *

Epitome

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(57) [Abstract]
[Technical problem] The heat exhanger tube of elevated-temperature corrosion resistance and the contaminant incineration exhaust gas use waste heat boiler which was especially excellent in intergranular corrosion-proof [elevated-temperature] nature is offered.
[Means for Solution] Cr: B:0.001-0.1 are contained 38-50% one sort in Mo and W or : [two sorts of] 0.1 - 2%, C:0.001 - 0.05%, and Mg:0.001-0.1%, contain the following (a) and/or (b) if needed further, the remainder consists of nickel and an unescapable impurity, and it is an unescapable impurity. Si: The heat exhanger tube constituted from a nickel-Cr radical alloy which has the presentation restricted to less than [0.1%], P:0.03% or less, and S:0.03% or less. (a) Rare earth elements : 1 of 0.001 - 0.1%, Y:0.001 - 0.1%, Zr:0.001-0.1%, and Hf:0.001-0.5% of sorts, two sorts or more. (b) 1 of Mn:0.01-1.0% and calcium:0.001-0.1% of sorts, two sorts.

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CLAIMS

[Claim(s)]
[Claim 1] By weight %, one sort Cr:38-50% and in Mo and W, or : [two sorts of] 0.1 - 2%, B:0.001-0.1 are contained C:0.001 - 0.05%, and Mg:0.001-0.1%. Si in which the remainder is contained as an unescapable impurity by consisting of nickel and an unescapable impurity, The heat exhanger tube of the contaminant incineration exhaust gas use waste heat boiler excellent in the elevated-temperature corrosion resistance characterized by constituting from a nickel-Cr radical alloy which has the presentation which restricted P and S to less than [Si:0.1%], P:0.03% or less, and S:0.03% or less, respectively.
[Claim 2] By weight %, one sort Cr:38-50% and in Mo and W, or : [two sorts of] 0.1 - 2%, B:0.001-0.1 are contained C:0.001 - 0.05%, and Mg:0.001-0.1%. Furthermore, rare earth elements : 0.001 - 0.1%, Y:0.001 - 0.1%, 1 of Zr:0.001-0.1% and Hf:0.001-0.5% of sorts and two sorts or more are contained. Si in which the remainder is contained as an unescapable impurity by consisting of nickel and an unescapable impurity, The heat exhanger tube of the contaminant incineration exhaust gas use waste heat boiler excellent in the elevated-temperature corrosion resistance characterized by constituting from a nickel-Cr radical alloy which has the presentation which restricted P and S to less than [Si:0.1%], P:0.03% or less, and S:0.03% or less, respectively.

[Claim 3] The heat exhanger tube of the contaminant incineration exhaust gas use waste heat boiler excellent in the elevated-temperature corrosion resistance characterized by constituting from a nickel-Cr radical alloy which contained 1 of Mn:0.01-1.0% and calcium:0.001-0.1% of sorts, and two sorts further into the nickel-Cr radical alloy according to claim 1 or 2.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the heat exhanger tube of elevated-temperature corrosion resistance and the contaminant incineration exhaust gas use waste heat boiler which was especially excellent in intergranular corrosion-proof [elevated-temperature] nature.
[0002]
[Description of the Prior Art] Generally, the waste heat boiler is installed in the contaminant incineration facility in order to use the elevated-temperature latent heat which exhaust gas has. moreover, HCl and SO2 with corrosive [strong / the heat exhanger tube which is the structural member of said waste heat boiler] Gas and Na2 SO4 etc. -- since it sets under the situation that it was exposed to a melting sulfate and the hot exhaust gas which contains corrosive products, such as fused salt ghosts, such as NaCl and KCl, further, and the parts of said sulfate, chloride, etc. deposited on the front face, the corrosion resistance outstanding ingredient is used for the manufacture.
[0003] As one of the corrosion resistance outstanding ingredients, it is (% shows weight % hereafter) at weight %, One sort in Mo and W or : [two sorts of] 0.1 - 2% are contained Cr:38-50%. Furthermore, the need is accepted. Rare-earth-elements:0.001-0.1%, Y:0.001 - 0.1%, 1 of Zr:0.1-3% and Hf:0.1-3% of sorts and two sorts or more are contained. C and N which are contained as an impurity are restricted to C:0.05% or less and N:0.04% or less, respectively, and the nickel-Cr radical alloy which has the presentation which the remainder becomes from nickel and other unescapable impurities is known (refer to JP,1-132732,A).
[0004]
[Problem(s) to be Solved by the Invention] Although the nickel-Cr radical alloy of this former given in JP,1-132732,A shows the corrosion resistance which was excellent to various kinds of acids strong corrosive HCl and strong corrosive SO2 by contaminant incineration Gas and Na2 SO4 etc. -- a melting sulfate -- In the bottom of the complicated situation that it is exposed to the hot exhaust gas which furthermore contains corrosive products, such as fused salt ghosts, such as NaCl and KCl, and the parts of said sulfate, chloride, etc. deposit on a front face Elevated-temperature corrosion resistance was insufficient for the heat exhanger tube of the contaminant incineration exhaust gas use waste heat boiler which did not show sufficient elevated-temperature corrosion resistance, therefore was constituted from this conventional nickel-Cr radical alloy, therefore its use life was short.
[0005]
[Means for Solving the Problem] Then, this invention person etc. develops the nickel-Cr radical alloy which has the elevated-temperature corrosion resistance which was excellent much more from the above viewpoints. The result of having inquired the heat exhanger tube of a contaminant incineration exhaust gas use waste heat boiler with a still longer use life being developed using the nickel-Cr radical alloy excellent in this elevated-temperature corrosion resistance, (b) If a nickel-Cr radical alloy given [conventional] in JP,1-132732,A is made to contain both Mg:0.001-0.1% and B:0.001-0.1 The heat exhanger tube of the

contaminant incineration exhaust gas use waste heat boiler which the nickel-Cr radical alloy whose intergranular corrosion-proof [elevated-temperature] nature improved was obtained while hot-working nature was excellent, and was constituted from this nickel-Cr radical alloy From the place in which intergranular corrosion-proof [elevated-temperature] nature is excellent compared with the heat exhanger tube constituted from a nickel-Cr radical alloy given [conventional] in JP,1-132732,A The elevated-temperature corrosion resistance in the inside of an exhaust gas ambient atmosphere improves further as a result, and the life of a heat exhanger tube is extended further. (b) Rare earth elements : if 1 of 0.001 - 0.1%, Y:0.001 - 0.1%, Zr:0.001-0.1%, and Hf:0.001-0.5% of sorts and two sorts or more are made to contain Since hot-working nature improves, it is desirable. (Ha) Content of 1 of Mn:0.01-1.0% and calcium:0.001-0.1% of sorts and two sorts obtained the research result of corrosion resistance improving further from the place where deoxidation of a nickel-Cr radical alloy is performed.

[0006] This invention is made based on the above-mentioned research result. Cr:38-50%, One sort in Mo and W or : [two sorts of] 0.1 - 2%, C:0.001 - 0.05%, B:0.001-0.1 are contained Mg:0.001-0.1%. Further The need is accepted. (a) rare-earth-elements:0.001-0.1%, Y:0.001 - 0.1%, Zr: 1 of 0.001-0.1% and Hf:0.001-0.5% of sorts, two sorts or more, (b) 1 of Mn:0.01-1.0% and calcium:0.001-0.1% of sorts, two sorts, As mentioned above, contain (a) and/or (b) and the remainder consists of nickel and an unescapable impurity. Si, P, and S which are contained as an unescapable impurity, respectively Less than [Si:0.1%], It has the description in the heat exhanger tube of the elevated-temperature corrosion resistance constituted from a nickel-Cr radical alloy which has the presentation restricted to P:0.03% or less and S:0.03% or less, and the contaminant incineration exhaust gas use waste heat boiler excellent in especially elevated-temperature intergranular corrosion nature.

[0007] The reason which limited the component presentation of the nickel-Cr radical alloy which constitutes the heat exhanger tube of this invention as above-mentioned is explained.

(a) Although it has the operation which raises high temperature strength while raising the elevated-temperature corrosion resistance and the elevated-temperature oxidation resistance hot in the condition of having coexisted with Mo and W over contaminant incineration exhaust gas for a CrCr component When the content became less than [Cr:38%], the effectiveness of a request to said operation was not acquired, but on the other hand, when Cr content exceeded 50%, it stiffened, and the content was desirably defined to 43 - 47% 38 to 50% from the place where a crack becomes easy to produce it at the time of fabrication. Few deposits of alpha phase of Cr radical are so desirable that there are in this presentation range, and the deposit of alpha phase of Cr radical can acquire the maximum corrosion resistance and workability by making it to 10% or less by surface ratio.

[0008] (b) Although both Mo and W these components had the operation which raises corrosion resistance in the condition of having dissolved on the base and having coexisted with Cr, the corrosion-resistant improvement effectiveness of a request [at less than 0.1%] of the content to said operation was not acquired, but since fabrication nature came to have fallen when the content exceeded 2% on the other hand, the content was desirably determined as 0.5 - 1.5% 0.1 to 2%.

[0009] (c) The content could not secure desired high temperature strength at less than 0.001%, but although CC component had the operation which raises high temperature strength, when the content of C component exceeded 0.05%, on the other hand, the amount of the carbide which exists in a grain boundary came to increase, and since advance of the intergranular corrosion by the fused salt ghost contained especially in elevated-temperature exhaust gas came to be promoted, the content was determined as 0.001 - 0.05%.

[0010] (d) The content since metallic compounds are generated on the grain community with which the effectiveness of a request of the content at less than 0.001% is not acquired although there is an operation which intergranular corrosion-proof [elevated-temperature] nature is raised for a MgMg component, and hot-working nature also raises, but the content exceeds 0.1% on the other hand and intergranular corrosion-proof [hot-working nature and elevated-temperature] nature comes to fall was desirably determined as 0.001 - 0.05% 0.001 to 0.1%.

[0011] (e) Although BB component had the operation which raises intergranular corrosion-proof [elevated-temperature] nature, since the effectiveness of a request of the content at less than 0.001% was not acquired, but boronizing **** was generated to the grain boundary where the content exceeds 0.1% on the other hand and it came to have fallen intergranular corrosion-proof [elevated-temperature] nature, the content was desirably determined as 0.001 - 0.01% 0.001 to 0.1%.

[0012] (f) rare earth elements, and Y, Zr and Hf, although they are made to contain if needed since these components have the operation which raises hot-working nature The hot-working disposition top effectiveness of the content's request of one of components at less than 0.001% is not acquired. If it is in

rare earth elements, and Y and Zr and is in Hf 0.1%, even if it exceeds 0.5% the other hand, hot-working nature from much more effecti ss of making it improving not being ac d The content was determined as rare-earth-elements:0.001-0.1%, Y:0.001 - 0.1%, Zr:0.001-0.1%, and Hf:0.001-0.5%.

[0013] (g) Although there is deacidification in Mn, CaMn, and calcium, and it adds by deoxidation by Mn and calcium addition if needed since the corrosion resistance of a nickel-Cr radical alloy is raised further If the effectiveness of a request to said operation is not acquired [less than 0.001%] by calcium component 0.01% of Mn component, but the content exceeds 1.0% of Mn component on the other hand and the content exceeds 0.1% of calcium component Since those deposit phases generated and hot-working nature and corrosion resistance fell, the content was defined to Mn:0.01-1.0% and calcium:0.001-0.1%, respectively.

[0014] (h) Although Si, P, S, Ti, and aluminum may be contained as an unescapable impurity unescapable impurity If toughness will come to fall if the content of Si component exceeds 0.1%, and P and S exceed P:0.03% and S:0.03%, respectively It comes to segregate to a grain boundary, and hot-working nature is reduced, and intergranular corrosion-proof [elevated-temperature] nature is also reduced, and if the content of Ti and aluminum exceeds 0.4%, respectively, hot-working nature will come to be spoiled. Therefore, Si, P, S, Ti, and aluminum must be limited to less than [Ti:0.4%] and less than [aluminum:0.4%] less than [Si:0.1%], P:0.03% or less, and S:0.03% or less, respectively.

[0015]

[Embodiment of the Invention] Below, an example explains the heat exhanger tube of this invention concretely. A nickel-Cr radical alloy molten metal with the component presentation shown in Tables 1-4 is prepared using the usual RF fusion furnace. Cast to an ingot, and perform hot forging to this ingot at the predetermined temperature within the limits of 1000-1250 degrees C, and it considers as diameter:65mm round bar material. subsequently, diameter [from this round bar material]: -- 60mmx thickness: -- heat exhanger tubes 1-5 were manufactured this invention heat exhanger tubes 1-35 and conventionally by beginning to delete in dimension of 5mm, respectively.

[0016] Subsequently, build into a waste heat boiler various kinds of heat exhanger tubes obtained as a result, and this waste heat boiler is installed in the contaminant incineration facility of throughput:200ton / day. Skin temperature of said heat exhanger tube : Operation of 1800 hours is performed on conditions (550 degrees C and exhaust gas temperature:670 degree C). While the heat exhanger tube after operation termination was taken out, the thickness in a hoop direction was measured where the ash content and the generation scale adhering to a front face are removed, and calculating the amount of the maximum thinning, it gazed at the cross-section microstructure of the surface section, the maximum intergranular corrosion die length was measured, and these results were shown in Table 5.

[0017]

[Table 1]

種別		成分組成 (重量%)										
		Cr	Mo	W	C	Mg	B	Si	P	S	その他	Ni+不純物
本発明伝熱管	1	38.2	0.5	0.9	0.034	0.042	0.005	0.045	0.015	0.008	-	残
	2	44.9	1.0	0.2	0.026	0.039	0.005	0.036	0.010	0.011	-	残
	3	49.8	0.5	1.7	0.036	0.028	0.002	0.078	0.016	0.017	-	残
	4	45.2	0.3	0.8	0.002	0.027	0.009	0.059	0.007	0.021	-	残
	5	45.6	0.6	0.7	0.047	0.025	0.006	0.008	0.019	0.012	-	残
	6	44.8	0.7	0.2	0.027	0.002	0.006	0.015	0.018	0.019	-	残
	7	44.7	0.5	0.4	0.030	0.098	0.007	0.026	0.025	0.014	-	残
	8	44.8	1.0	0.2	0.025	0.026	0.002	0.032	0.009	0.016	-	残
	9	44.9	0.3	0.6	0.039	0.036	0.097	0.039	0.016	0.023	-	残
	10	45.2	0.2	-	0.028	0.029	0.004	0.043	0.020	0.018	-	残

[0018]

[Table 2]

種別		成分組成 (重量%)										
		Cr	Mo	W	C	Mg	B	Si	P	S	その他	Ni+不純物
本発明伝熱管	11	44.8	1.8	-	0.027	0.032	0.006	0.018	0.015	0.019	-	残
	12	44.7	-	0.2	0.030	0.048	0.007	0.025	0.016	0.014	-	残
	13	44.8	-	1.9	0.025	0.026	0.002	0.009	0.002	0.016	-	残
	14	44.9	0.1	0.1	0.029	0.036	0.007	0.018	0.009	0.023	-	残
	15	45.2	1.2	0.7	0.028	0.029	0.004	0.020	0.003	0.018	-	残
	16	46.6	1.0	0.5	0.021	0.033	0.008	0.074	0.009	0.011	La:0.045, Ce:0.021	残
	17	45.8	0.6	1.0	0.019	0.029	0.005	0.015	0.011	0.024	Y:0.071	残
	18	45.6	-	1.5	0.036	0.031	0.009	0.009	0.012	0.009	Zr:0.068	残
	19	45.1	-	1.2	0.028	0.021	0.009	0.045	0.014	0.019	Hf:0.15	残
	20	46.4	1.4	-	0.022	0.029	0.006	0.016	0.011	0.012	La:0.078, Y:0.023	残

[0019]

[Table 3]

種別		成分組成 (重量%)										
		Cr	Mo	W	C	Mg	B	Si	P	S	その他	Ni+不純物
本発明伝熱管	21	44.4	1.6	-	0.027	0.024	0.008	0.012	0.013	0.011	Ce:0.078, Hf:0.091	残
	22	45.1	0.9	0.7	0.023	0.031	0.004	0.009	0.020	0.012	La:0.066, Zr:0.047	残
	23	46.5	0.8	0.3	0.038	0.029	0.009	0.021	0.025	0.022	Y:0.041, Hf:0.11	残
	24	44.2	1.4	0.2	0.025	0.027	0.003	0.011	0.029	0.024	La:0.033, Y:0.0071, Hf:0.083	残
	25	45.2	0.6	1.2	0.029	0.030	0.009	0.012	0.029	0.015	Ce:0.012, Y:0.074, Zr:0.074	残
	26	44.8	1.2	-	0.034	0.045	0.008	0.012	0.022	0.011	La:0.0074, Hf:0.082, Zr:0.056	残
	27	45.8	1.4	-	0.028	0.032	0.002	0.039	0.018	0.021	Ce:0.0074, Hf:0.082, Zr:0.0056, Y:0.0047	残
	28	46.0	1.0	0.5	0.019	0.034	0.007	0.023	0.024	0.008	Mn:0.82	残
	29	45.6	0.8	0.8	0.021	0.025	0.008	0.021	0.016	0.012	Ca:0.081	残
	30	45.2	-	1.3	0.036	0.029	0.007	0.016	0.009	0.021	Mn:0.14, Ca:0.031	残

[0020]

[Table 4]

種別		成分組成（重量%）										
		Cr	Mo	W	C	Mg	B	Si	P	S	その他	Ni+不純物
本発明伝熱管	31	44.9	1.1	-	0.028	0.030	0.002	0.048	0.020	0.013	Mn:0.66, Y:0.062, Ca:0.072	残
	32	45.1	0.8	0.5	0.033	0.033	0.003	0.028	0.020	0.010	Mn:0.72, La:0.092, Y:0.034	残
	33	45.3	0.5	0.7	0.080	0.035	0.004	0.043	0.015	0.015	Ca:0.042, Hf:0.22, Y:0.054	残
	34	45.3	0.6	0.3	0.044	0.041	0.008	0.022	0.013	0.012	Mn:0.32, La:0.063, Hf:0.12, Ca:0.078, Y:0.026	残
	35	45.8	0.9	0.4	0.032	0.029	0.007	0.014	0.017	0.011	Mn:0.20, Y:0.013, Hf:0.098, Ca:0.019, Zr:0.025	残
従来伝熱管	1	39.7	1.5	0.2	0.031	-	-	-	-	-	N:0.032	残
	2	45.3	0.6	0.5	0.028	-	-	-	-	-	N:0.025	残
	3	45.5	0.4	1.1	0.022	-	-	-	-	-	N:0.019	残
	4	46.2	-	1.7	0.013	-	-	-	-	-	N:0.027	残
	5	45.6	1.5	-	0.024	-	-	-	-	-	N:0.030	残

（＊印：本発明範囲外）

[0021]
[Table 5]

種別		最大減肉量（mm）	最大粒界腐食長さ（mm）	種別		最大減肉量（mm）	最大粒界腐食長さ（mm）	種別		最大減肉量（mm）	最大粒界腐食長さ（mm）
本発明伝熱管	1	0.29	0.11	本発明伝熱管	16	0.25	0.09	本発明伝熱管	31	0.24	0.07
	2	0.25	0.08		17	0.25	0.08		32	0.25	0.08
	3	0.28	0.10		18	0.26	0.09		33	0.25	0.08
	4	0.26	0.10		19	0.26	0.09		34	0.23	0.07
	5	0.26	0.09		20	0.26	0.09		35	0.23	0.07
	6	0.26	0.09		21	0.26	0.09	従来伝熱管	1	0.38	0.15
	7	0.27	0.10		22	0.25	0.09		2	0.37	0.13
	8	0.26	0.09		23	0.25	0.08		3	0.37	0.15
	9	0.27	0.09		24	0.25	0.09		4	0.38	0.16
	10	0.28	0.10		25	0.25	0.09		5	0.35	0.13
	11	0.28	0.11		26	0.25	0.09				
	12	0.29	0.10		27	0.26	0.08				
	13	0.28	0.10		28	0.24	0.08				
	14	0.28	0.09		29	0.24	0.08				
	15	0.28	0.09		30	0.24	0.07				

[0022]
[Effect of the Invention] even if this invention heat exhanger tubes 1-35 are conventionally exposed to a hot contaminant incineration exhaust gas ambient atmosphere between durability compared with heat exhanger tubes 1-5, there are few amounts of the maximum thinning, and the result shown in Tables 1-5 shows that the maximum intergranular corrosion die length is markedly alike, and shows the elevated-temperature corrosion resistance which was excellent from the short place, and the especially excellent intergranular corrosion-proof [elevated-temperature] nature.
[0023] As mentioned above, since the elevated-temperature corrosion resistance in which the heat exhanger tube of this invention that added the minute amount excelled before much more in Mg and B is shown, much more reinforcement of the heat exhanger tube of the waste heat boiler for using the waste heat by contaminant incineration effectively becomes possible, and it can greatly contribute to improvement in the technique of the waste heat boiler for using the waste heat by contaminant incineration

effectively.

[Translation done.]